Journal of Photochemistry and Photobiology A: Chemistry 311 (2015) 193–198

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Photochemistry of P3HT and $PC_{60}BM$ in toluene solution: Evidence of T–T energy transfer

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ARTICLE INFO

Article history:
Received 30 May 2015
Received in revised form 2 July 2015
Accepted 4 July 2015
Available online 7 July 2015

Keywords:
$PC_{60}BM$
P3HT
Triplet state
Triplet energy transfer
Flash photolysis
Fluorescence

ABSTRACT

Photochemical properties of regioregular poly(3-hexylthiophene) (P3HT), fullerene derivative [6,6]-phenyl C61-butyric acid methyl ester ($PC_{60}BM$) and their 1:1 mixture in argon-saturated toluene solution were studied by optical spectroscopy and nanosecond laser flash photolysis ($\lambda_{ex} = 532$ nm). Separate excitation of components leads to formation of corresponding triplet state of fullerene ($^3PC_{60}BM^*$, $\lambda_{max} = 710$ nm, $\varepsilon_{max} = 22400\ M^{-1}\ cm^{-1}$, $\varphi_T = 0.29$) and polymer ($^3P3HT^*$, $\lambda_{max} = 850$ nm, $\varepsilon^{750\,nm} \leq 10^5\ M^{-1}\ cm^{-1}$, $\varphi_T \geq 0.19$). Excitation of P3HT/$PC_{60}BM$ mixture leads to effective energy transfer from $^3P3HT^*$ to the ground state of fullerene with a formation of $^3PC_{60}BM^*$. No evidence of ion-radical $P3HT^{+\bullet}$ and $PC_{60}BM^{-\bullet}$ formation was obtained though electron transfer between $^3P3HT^*$ and $^1PC_{60}BM$ is energetically favorable in studied system. Presumably ultrafast back electron transfer takes place in geminate $P3HT^{+\bullet}/PC_{60}BM^{-\bullet}$ pair with regeneration of the ground states of P3HT and $PC_{60}BM$.

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1. Introduction

Conductive polymers and fullerenes attract undiverted attention now because of possible use of these materials in organic photovoltaics [1–5]. Photochemical processes involving these materials are widely studied mostly in solid polymer/fullerene composites, which are used as active layer of organic solar cells [6]. The majority of transient absorption studies of such composites are devoted to charge formation [7,8] and recombination [9–13]. In some works the triplet state [14] formation is studied [7,15–18]. Ultrafast transient absorption spectroscopy also allows to observe exciton dynamics in polymer/fullerene blends [19,20].

Light-induced processes in liquid solutions of conductive polymers, mainly poly(3-hexylthiophene) (P3HT) [21,22], the benchmark polymer for organic photovoltaics, and fullerenes [23] were addressed only in few works where dynamics of the excited states of these molecules was studied. Also, photodegradation of polymers was observed in several works [24,25], but possible influence of fullerene on this process was not studied.

The laser flash photolysis study of the solutions containing conjugated polymer and C_{60} revealed the efficient triplet states formation and energy transfer from triplet states of polymer to fullerene [26]. Photochemical processes in solutions containing fullerenes C_{60}/C_{70} and oligothiophenes of different length/polythiophene were studied in Ref. [27]. The electron transfer involving either triplet state of fullerene or triplet state of oligothiophenes/polythiophene and triplet–triplet energy transfer between fullerene and oligothiophenes/polythiophene were observed. The solvent dependence of the reaction pathway was observed in Ref. [27] in C_{60}/polythiophene solution. In polar solvent the electron transfer was dominant; while in nonpolar solvent mainly energy transfer took place. The reason is the smaller stabilization energy of radical-ion pair in nonpolar solvent [27].

Nevertheless, to our knowledge, photochemical processes in solutions containing both P3HT and $PC_{60}BM$, the most popular combination in organic photovoltaics, have not been reported yet. However, these processes may be of importance for production of organic solar cells. This is because polymer/fullerene thin film blends for these devices are usually casted from such solutions [28–30], and during the preparation and production they are illuminated for some extent. Therefore, the possibility of photochemical processes in solutions should be studied.

In the present work light-induced formation of the triplet state of P3HT and $PC_{60}BM$, as well as triplet–triplet energy transfer in this system were studied by nanosecond laser flash photolysis method. The rates of the corresponding processes, the quantum

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http://dx.doi.org/10.1016/j.jphotochem.2015.07.002
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yields of the triplet states of P3HT and $PC_{60}BM$ and their absorption spectra are determined. The extinction coefficients for these triplet states are accurately measured.

2. Materials and methods

$PC_{60}BM$ was purchased from Aldrich. Regioregular P3HT with molecular weight approximately 20–40 kDa was received from BASF (Sepiolid P200). Both $PC_{60}BM$ and P3HT were used without further purification. Unless otherwise specified, all photochemical experiments were performed in a 1 cm quartz cell in argon-saturated toluene (HPLC grade) solutions, temperature 298 K and atmospheric pressure.

UV absorption spectra were recorded using an Agilent 8453 spectrophotometer (Agilent Technologies). The fluorescence spectra and kinetics were measured on a FLSP920 spectrofluorimeter (Edinburg Instrument). As excitation sources ozone free xenon lamp Xe900 (λ_{ex} = 375 nm) and diode laser EPL-375 (λ_{ex} = 375 nm, pulse duration of 75 ps, Edinburg Instruments) were used, correspondingly. Kinetic curves were fitted by iterative reconvolution of one exponential function with the instrument response function, which allows to determine fluorescence lifetimes as short as 50 ps.

The laser flash photolysis setup based on LS-2137U Nd:YAG laser (Lotis TII, Belarus) with excitation wavelength of 532 nm, pulse duration of 5–6 ns, illumination spot area of 0.07 cm^2, and energy per pulse up to 5 mJ was used for the time-resolved measurements in visible region (400–800 nm); the device was similar to that described in previous work [31]. Time resolution of the setup was ca. 50 ns. Laser intensity was measured by means of SOLO 2 laser power meter (Gentec EO).

Nanosecond time-resolved absorption spectroscopy experiments in near-IR (940–1200 nm) were performed using the original experimental set-up constructed recently in Institute of Chemistry of Saint Petersburg State University. The excitation source was the second harmonic (532 nm, 7 ns, 1.5 mJ per pulse, 10 Hz) of an Nd:YAG laser (SOL instruments Ltd. LF117). A 150 W xenon arc lamp (Newport) was used as the probe source. Transient absorption signals were measured in the transverse geometry in which the probe was made to pass through a 1 cm quartz cell filled with the sample solution. The probe and pump beams had square profiles of 7×7 mm size at the sample position. After passage through the samples, the probe beam was dispersed through a double monochromator (Standa MSA-130) and detected using a photomultiplier tube (Hamamatsu H10330A-75) connected to a digital oscilloscope (Agilent Technologies InfiniiVision DS07054B). Data from the digital oscilloscope (3000 averaged scans) were analyzed using Origin 9.0 software.

3. Results and discussion

3.1. Absorption spectra of P3HT, $PC_{60}BM$ and their mixture in toluene solution

Absorption spectra of toluene solutions of P3HT, $PC_{60}BM$ and 1:1 mixture of P3HT/$PC_{60}BM$ at room temperature are shown in Fig. S1. P3HT exhibit broad single band at 450 nm with absorption coefficient (referred to moles of the P3HT monomer unit, Mw = 169) equals to 6700 $M^{-1}\,cm^{-1}$. Close value was obtained by Cook et al. [22] in chlorobenzene (λ_{max} = 455 nm, ε_{max} = 7800 $M^{-1}\,cm^{-1}$). $PC_{60}BM$ spectrum coincides well with published in [23] with λ_{max} = 500 nm and ε_{max} = 1500 $M^{-1}\,cm^{-1}$. Absorption spectrum of the P3HT/$PC_{60}BM$ 1:1 mixture is an algebraic sum of spectra of separate reagents which indicates absence of interaction between unexcited components (similar to that shown in [27] for C_{60}–P3HT mixture). It worth to note, that the main part of 532 nm light in mixture was absorbed by P3HT (80%).

3.2. Quenching of P3HT fluorescence by $PC_{60}BM$

In order to estimate probability of ^{1}P3HT* interaction with $PC_{60}BM$ in toluene solution the quenching of P3HT (0.25 mg/ml) fluorescence by $PC_{60}BM$ (0–7.4 mM) were studied (Fig. S2a,b). The P3HT fluorescence decay without $PC_{60}BM$ is practically mono-exponential with the characteristic time of 500 ps in a good agreement with literature data [22]. Linear increase of P3HT fluorescence decay rate with the increase of $PC_{60}BM$ concentration allow one to determine corresponding quenching rate constant, $k_q = 1.3 \times 10^{11}\,M^{-1}\,s^{-1}$ (Fig. S2c). This value is an order of magnitude larger than diffusion-limited reaction rate for small molecules in toluene. Such a large value of apparent quenching rate constant is often explained by association of fluorophore and quencher molecules. However, strong interaction between P3HT and $PC_{60}BM$ molecules in toluene solution is unlikely because no new bands or shift of existing bands were observed in absorption spectra upon mixing P3HT and $PC_{60}BM$ solutions (data not shown). High quenching rate constant can be cause by large size of P3HT molecule and fast intramolecular excitation diffusion within P3HT chain. The reaction rate constant of similar magnitude was observed for diffusion-controlled triplet energy transfer from biphenyl to conjugated polymer MEH-PPV [32]. Overall, this data allow one to conclude that at concentration of $PC_{60}BM$ used in laser flash photolysis experiments ($<1.5 \times 10^{-4}$ M) energy and electron transfer from ^{1}P3HT* to $PC_{60}BM$ could be neglected.

3.3. Laser flash photolysis of P3HT

Excitation of argon-saturated solution of P3HT in toluene leads to instant formation of wide transient absorption (TA) band with maximum in near-IR region (>800 nm, Fig. 1a) which decays in microsecond time scale with characteristic time about 14 μs (Fig. 1b). The presence of dissolved oxygen decreases the transient lifetime up to 0.16 μs. This fact and results of Cook et al. [22] allows to assign this wide band to T–T absorption of polymer (^{3}P3HT*, λ_{max} = 850 nm in dichlorobenzene [22,27]). The monoexponential TA decay kinetics typical for triplet states on conjugated polymers [33] was observed. Yield of T–T absorption at 750 nm exhibits linear dependence on excitation energy at laser intensity less than

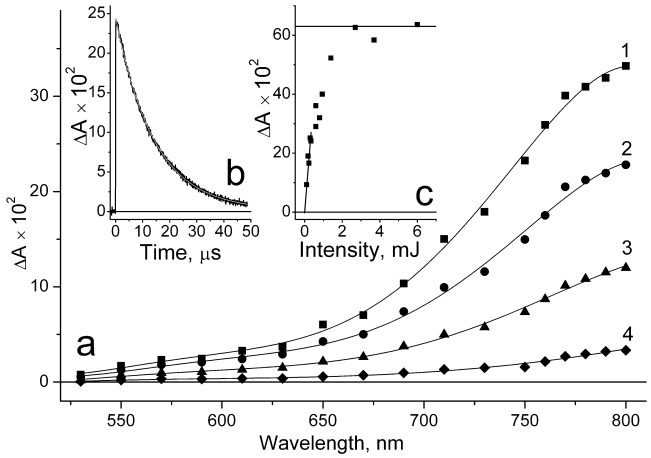

Fig. 1. (a) TA spectra of P3HT (0.25 g/L) in argon-saturated toluene solution recorded at 0.05 (1), 4 (2), 10 (3) and 22 (4) μs after the laser excitation (532 nm, 0.23 mJ/pulse, 95% of light was absorbed by P3HT). (b) The kinetic curve of transient absorption decay at 750 nm with the best exponential fit with τ = 14 μs. (c) Dependence of the yield of T–T absorption at 750 nm upon laser excitation energy.

1 mJ/pulse (Fig. 1c) which allows to estimate the product $\varphi_T\varepsilon_T^P = 1.9\times10^4\,M^{-1}\,cm^{-1}$. At excitation energies higher than 2 mJ/pulse the yield of the T–T absorption (750 nm) reaches its ultimate value of 0.63. This probably indicates that at high excitation energies each P3HT chain bears the triplet excitation and allows one to estimate the "concentration" of ^{3}P3HT* = 6×10^{-6} M using the value of $\varepsilon_T^P = 10^5\,M^{-1}\,cm^{-1}$ determined below. The saturation of T–T absorption with excitation energy growth is probably caused by fast triplet–triplet annihilation when two triplet excitations are localized at the same P3HT chain. As "concentration" of thiophene monomers in the experimental conditions was 1.48×10^{-3} M one can estimate that ultimate T–T absorption value corresponds to production of one triplet state per approximately 250 monomer thiophene units. This is in good agreement with the average P3HT chain length in the sample (about 200 monomers).

3.4. Laser flash photolysis of $PC_{60}BM$

Excitation of argon-saturated solution of $PC_{60}BM$ in toluene leads to instant formation of a wide TA band with maximum at 710 nm (Fig. 2) which decays in microsecond time scale (Fig. 2, inset). This finding is in the good agreement with work of Wang et al. where this transient absorption was assigned to the T–T absorption of fullerene [23]. Yield of T–T absorption (Fig. 3a) exhibits linear dependence on excitation energy at laser intensity less than 1 mJ/pulse which allows to estimate the product $\varphi_T\varepsilon_T^f = 9.7\times10^3\,M^{-1}\,cm^{-1}$. The same value was obtained in analogous experiment with 355 nm excitation. These results are in good agreement with data of Wang et al. where product of $\varphi_T\varepsilon_T^f = 1.2\times10^4\,M^{-1}\,cm^{-1}$, $\varepsilon_T^f = 2.24\times10^4\,M^{-1}\,cm^{-1}$ and $\varphi_T = 0.54$ were determined under 355 nm excitation of $PC_{60}BM$ solution in toluene [23].

The linear dependence of observed rate constant of T–T absorption decay at 710 nm ($k_{obs}^{710\,nm}$) on initial concentration of the $^3PC_{60}BM^*$ indicates that this state decays both in quenching of residual oxygen and T–T annihilation (Fig. 3b):

$$^3PC_{60}BM^* - (O_2) \rightarrow {}^1PC_{60}BM$$

$$^3PC_{60}BM^* + {}^3PC_{60}BM^* \rightarrow {}^1PC_{60}BM^* + {}^1PC_{60}BM,\ k_{T-T}$$

Using known value of $\varepsilon_T^f = 2.24\times10^4\,M^{-1}\,cm^{-1}$ [23] one can determine the rate constant of T–T annihilation, $k_{T-T} = 3.5\times10^9$ $M^{-1}\,s^{-1}$ which is close to diffusion one and to that previously determined for fullerene C_{60}, $k_{T-T} = 5.4\times10^9\,M^{-1}\,s^{-1}$ [34].

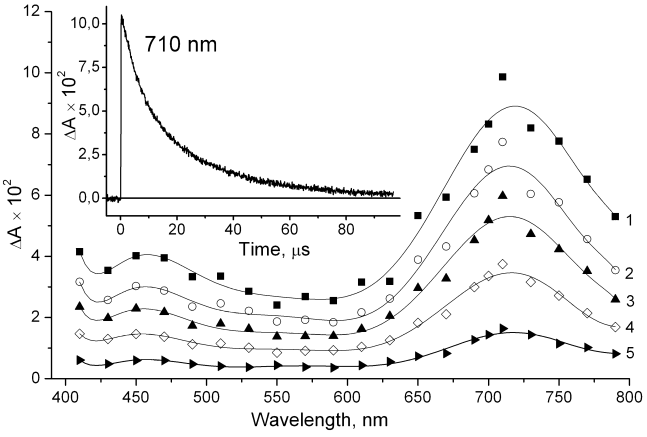

Fig. 2. TA spectra of $PC_{60}BM$ (0.25 g/L) in argon-saturated toluene solution recorded at 0.1 (1), 4 (2), 8 (3), 16 (4) and 36 (5) μs after the laser excitation (532 nm, 0.4 mJ/pulse, 55% of light was absorbed by $PC_{60}BM$). Insert—the kinetic curve of transient absorption decay at 710 nm.

4.1. Laser flash photolysis of P3HT/ $PC_{60}BM$ 1:1 mixture.

The measurements of transient absorption of 1:1 P3HT/$PC_{60}BM$ mixture in argon-saturated toluene were done both in the visible (500–800 nm) and the near-IR (950–1200 nm) regions. Excitation of the sample solution leads to formation of transient absorption which is a sum of T–T absorption spectra of the components (Fig. 4). At times <4 μs the main contribution to TA spectrum belongs to ^{3}P3HT*. At times >10 μs TA spectrum is fully identical to T–T absorption spectrum of fullerene (Fig. S3). No manifestation of any presence of ion-radical species $P3HT^{+\bullet}$ (λ_{max} = 740 nm for close analogue P3OT was reported in [27]) and $PC_{60}BM^{-\bullet}$ (λ_{max} = 1020 nm [35]) was observed. Kinetics of TA decay in whole range of wavelengths could be adequately fitted by biexponential law (Fig. 4, insert):

$$\Delta A(t) = A_1\exp(-k_{obs1}t) + A_2\exp(-k_{obs2}t) \quad (1)$$

where "1" and "2" stand for decay of polymer and fullerene triplet state, accordingly; A_1, A_2 and k_{obs1}, k_{obs2} are corresponding amplitudes and observed rate constants. For simplicity complex decay of fullerene triplet state was simulated by exponential law. This is possible for two main reasons: (i) low excitation energy was used which suppressed T–T annihilation (>75% of $^3PC_{60}BM^*$ decays monoexponentially by quenching by residual oxygen), (ii) at short time range mixed first and second order kinetics could be adequately fitted by single exponential decay. It worth to note that yield of fullerene triplet state at 710 nm (which is related with A_2 amplitude) is much higher than one calculated from known value of light intensity directly absorbed by fullerene and decay of ^{3}P3HT* matches the grow-in of $^3PC_{60}BM^*$.

Two mechanisms explaining the additional $^3PC_{60}BM^*$ formation in reaction between excited states of P3HT and fullerene molecule could be proposed:

M1. T–T energy transfer. Realization of this mechanism was demonstrated in the laser flash photolysis study of the solutions of conjugated polymer and C_{60} in para-xylene and ortho-dichlorobenzene [26].

M2. Photoinduced electron transfer (PET) with formation of ion-radical pair followed by ultrafast back electron transfer (BET) in the geminate pair with formation of $^3PC_{60}BM^*$ and ground state of polymer. Evidence of direct ET was demonstrated for polythiophene/C_{60} solution in benzonitrile [27] where both long-lived $P3OT^{+\bullet}$ and $C_{60}^{-\bullet}$ were detected by nanosecond flash photolysis.

Fig. 5 shows the schematic energy diagram of P3HT/$PC_{60}BM$ system. The ground state of polymer and fullerene is assumed to have zero energy. Energies of $^1PC_{60}BM^*$ and $^3PC_{60}BM^*$ states were taken from the work [17]; energy of ^{1}P3HT* in chlorobenzene solution was determined in [22]. The energy of ^{3}P3HT* has not been reported in the literature, therefore the triplet state energy of the very similar polymer P3OT in benzene [36] was taken as an estimation. Energy of charge transfer state was estimated using the following equation:

$$\frac{E_{CT} = E_{HOMO}(P3HT) - E_{LUMO}(PC_{60}BM) - e^2}{a\varepsilon_s} \quad (2)$$

The values of HOMO of P3HT and LUMO of $PC_{60}BM$ were measured by cyclic voltammetry in solutions of P3HT in toluene and $PC_{60}BM$ in chlorobenzene [36]. In the estimation of the Coulomb interaction energy between charges in toluene solution (dielectric constant ε_s = 2.38) the distance a was assumed to be

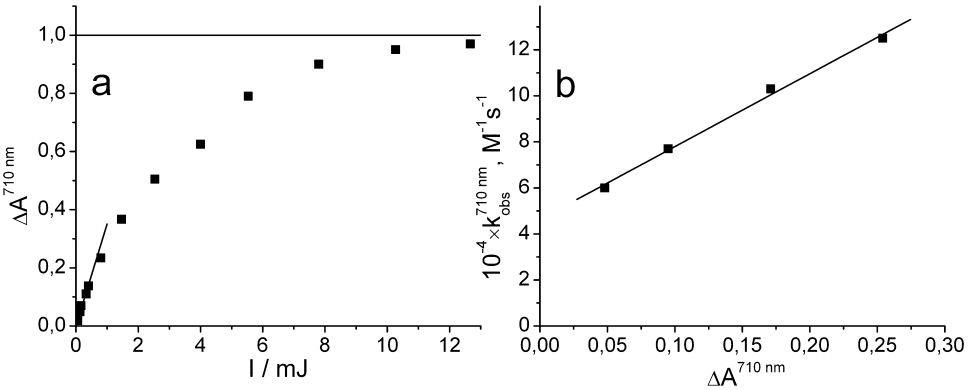

Fig. 3. Laser (532 nm) flash photolysis of $PC_{60}BM$ (0.25 g/L) in argon-saturated toluene solution. (a) Dependence of the T–T absorption yield at 710 nm on excitation energy. (b) Dependence of $k_{obs}^{710\,nm}$ on initial absorption of the fullerene triplet state at 710 nm.

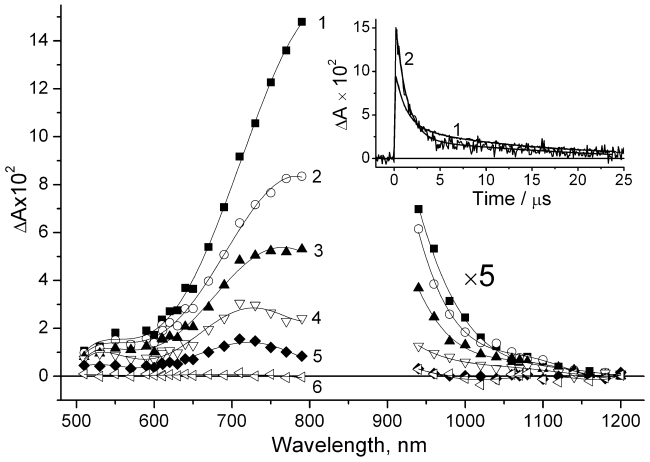

Fig. 4. TA spectra recorded at 0.1 (1), 0.8 (2), 1.6 (3), 4 (4), 13 (5) and 60 (6) μs after the laser excitation of 1:1 P3HT/$PC_{60}BM$ mixture in argon-saturated toluene solution. Note that data in near-IR region is multiplied by factor of 5 for better visualization. Concentrations of fullerene and polymer are 0.125 g/L, excitation energy 0.21 mJ/pulse, 17% of light was absorbed by $PC_{60}BM$ and 67%—by P3HT. Insert—the kinetic curves of TA decay at 710 (1) and 790 (2) nm with the best biexponential fit according to Eq. (1).

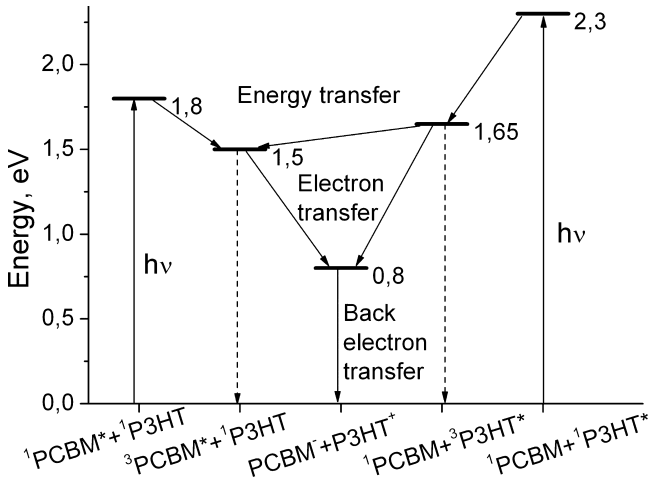

Fig. 5. Schematic energy diagram for electron and energy transfer processes between P3HT and $PC_{60}BM$. Zero energy corresponds to ^{1}P3HT + $^1PC_{60}BM$ state.

about 2 nm. In geminate electron/hole pair the distance between charges is expected to be smaller, but the P3HT cation radical is known to be distributed over several monomers [38], therefore the average distance is increased.

Thermodynamic estimations show that mechanism M2 could not be realized, because it is energetically unfavorable, and recombination of $P3HT^{+\bullet}/PC_{60}BM^{-\bullet}$ pair (if it appears) should lead to formation of the ground states of both reagents (Fig. 5). It should be noted that even if Coulomb interaction energy is not taken into account, the energy of charge transfer state is not sufficient for $^3PC_{60}BM^*$ state formation. The difference between our findings and results of [27] could be explained by the smaller stabilization energy of ion-radical pair $P3HT^{+\bullet}/PC_{60}BM^{-\bullet}$ in nonpolar toluene leading to ultrafast BET and zero charge separation quantum yield, similar to the results reported in [27] for 3T oligothiophene/C_{60} solution in a mixture solvent of benzonitrile and ortho-dichlorobenzene (1:1). Also the slight decrease of charge separation quantum yield with the reduction of solvent polarity observed in [27] proves the stabilization of radical ions in more polar solvent. So in our system mechanism M1 is responsible for formation of additional $^3PC_{60}BM^*$.

It was observed that life-time of polymer triplet state decreases with increase of fullerene concentration in solution. At the same time decay of fullerene triplet state is not affected by presence of polymer. From linear dependence of k_{obs1} at 750 nm on fullerene concentration (Fig. 6a) the rate constant of ^{3}P3HT* quenching was calculated, $k_q = 5.5 \times 10^9\ M^{-1}\ s^{-1}$ which is in a good agreement with known literature data [27].

It should be noted, that PET from ^{1}P3HT* to $PC_{60}BM$ or from P3HT to $^1PC_{60}BM^*$ is energetically favorable in our system (Fig. 5) but it is kinetically impossible, because characteristic time of PET (≈100 ns, based on above determined quenching rate constant ($1.3 \times 10^{11}\ M^{-1}\ s^{-1}$) and typical concentration of reagents) is two orders of magnitude longer than lifetime of the singlet states of both $^1PC_{60}BM^*$ (≈1.5 ns [23]) and ^{1}P3HT* (≈0.5 ns [22]). So this mechanism must be ruled out in our system.

The absence of light-induced charge separation for P3HT/$PC_{60}BM$ mixture dissolved in toluene is in sharp contrast with P3HT/$PC_{60}BM$ solid composite, for which the yield of separated charges is chose to unity [39,40]. While the mechanism of light-induced charge separation in P3HT/$PC_{60}BM$ bulk heterojunction blend is not completely understood now [41–45], the difference between the P3HT–$PC_{60}BM$ mixture in solution and solid state P3HT/$PC_{60}BM$ composite can be explained. In composites, positive and negative charges have a good chance to jump into the neighboring P3HT or $PC_{60}BM$ molecules, respectively, and thus to move further apart. On the contrary, in liquid solution the

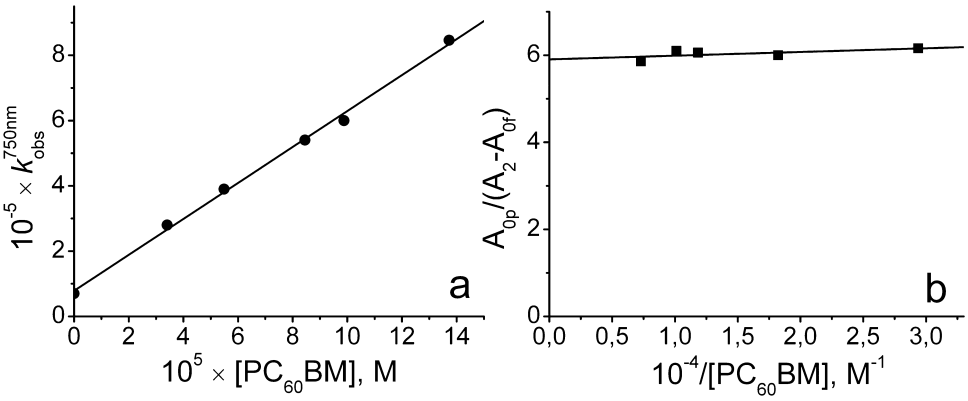

Fig. 6. (a) dependence of k_{obs1} at 750 nm upon $PC_{60}BM$ concentration. (b) Dependence of $A_{0p}/(A_2 - A_{0f})$ at 750 nm on inverse $PC_{60}BM$ concentration.

movement of charges is governed by diffusion, so Coulomb attraction precludes charge separation and enhances recombination. The estimated energy of Coulomb attraction in geminate ion-radical pair $P3HT^{+\bullet}/PC_{60}BM^{-\bullet}$ is about 0.2 eV which is much larger than thermal energy kT. Therefore, the probability of the ion-radical pair to separate is very low.

Thus, main (photo) chemical reactions taking place upon P3HT–$PC_{60}BM$ mixture excitation could be presented by the following kinetic scheme:

$$^1P3HT - hv,\ ISC \rightarrow {}^3P3HT^* \quad (3)$$

$$^1PC_{60}BM - hv,\ ISC \rightarrow {}^3PC_{60}BM^* \quad (4)$$

$$^3P3HT^* + {}^1PC_{60}BM - k_{En} \rightarrow {}^1P3HT + {}^3PC_{60}BM^* \quad (5a)$$

$$^3P3HT^* + {}^1PC_{60}BM - k_{El} \rightarrow P3HT^{+\bullet} + PC_{60}BM^{-\bullet} - k_{BET} \rightarrow {}^1P3HT + {}^1PC_{60}BM \quad (5b)$$

$$^3P3HT^* - k_p \rightarrow {}^1P3HT \quad (6)$$

$$^3PC_{60}BM^* - k_{obs2} \rightarrow {}^1PC_{60}BM, \quad (7)$$

where k_{En}, k_{El} are rate constants of energy and electron transfer ($k_q = k_{En} + k_{El}$), k_{BET} is rate constant of back electron transfer, k_{obs2} is the observed rate constant of $^3PC_{60}BM^*$ decay in processes of T–T annihilation and residual oxygen quenching, k_p—pseudo-first order rate constant of $^3P3HT^*$ reaction with residual oxygen. Analytical solution of differential equations corresponding to scheme (3–7) gives the following evolution of $^3PC_{60}BM^*$ and $^3P3HT^*$ absorbance:

$$\Delta A_P(t) = A_{0p}\exp(-k_{obs1}t) \quad (8)$$

$$\Delta A_F(t) = \left[A_{0f} + \frac{\varepsilon_T^f}{\varepsilon_T^p}\frac{k'_{En}A_{0p}}{k'_{En}k_{obs2}}\right]\exp(-k_{obs2}t) - \frac{\varepsilon_t^f}{\varepsilon_T^p}\frac{k'_{En}A_{0p}}{k_{obs1}-k_{obs2}}\exp(-k_{obs1}t), \quad (9)$$

where A_{0p}, εA_{0f} are the initial absorbance of $^3P3HT^*$ and $^3PC_{60}BM^*$, accordingly; $k_{obs1} = k_p + (k_{En} + k_{El})[^1PC_{60}BM]$ and $k_{En}' = k_{En}[^1PC_{60}BM]$. A_{0p} and A_{0f} could be calculated from known optical density of the mixture at 532 nm, percentage of light absorbed by each component and $\varphi_T\varepsilon_T{}^f$, $\varphi_T\varepsilon_T{}^P$ values determined above. Combination of Eqs. (7) and (8) gives the equation totally identical to Eq. (1) where:

$$A_1 = A_{0p}\left(1 - \frac{\varepsilon_p^f}{\varepsilon_T^p}\frac{k'_{En}}{k_{obs1}-k_{obs2}}\right); A_2 = A_{0f} + \frac{\varepsilon_T^f}{\varepsilon_T^p}\frac{k'_{En}A_{0p}}{k_{obs1}-k_{obs2}} \quad (10)$$

Expression for A_2 could be rewritten as:

$$\frac{A_{0p}}{A_2 - A_{0f}} = \frac{\varepsilon_T^P}{\varepsilon_T^f}\left(1 + \frac{k_{el}}{k_{en}}\right) + \frac{\varepsilon_T^P}{\varepsilon_T^f}\left(\frac{k_p - k_{obs2}}{k_{en}}\right)\frac{1}{[^1PC_{60}BM]} \quad (11)$$

Fig. 6b demonstrate dependence of $A_{0p}/(A_2 - A_{0f})$ at 750 nm on inverse concentration of $PC_{60}BM$ which allows to calculate $\varepsilon_T^P/\varepsilon_T^f(1 + k_{el}/k_{en})$ ratio ≈5.9. Small slope is due to the fact that $k_p - k_{obs2} = 0$ in the experimental conditions used. As k_{el}/k_{en} ratio is unknown it is only possible to estimate upper value of $\varepsilon_T{}^P$ (if $k_{el} = 0$). Using known value of $\varepsilon_T{}^f(750\,nm) = 1.74 \times 10^4\,M^{-1}\,cm^{-1}$ (calculated from $\varepsilon_T{}^f(750\,nm)/\varepsilon_T{}^f(710\,nm) = 0.78$ and $\varepsilon_T{}^f(710\,nm) = 2.24 \times 10^4\,M^{-1}\,cm^{-1}$ [23]) one can estimate $\varepsilon_T{}^P(750\,nm) \leq 10^5\,M^{-1}\,cm^{-1}$. Using this value and determined above product of $\varphi_T\varepsilon_T{}^P = 1.9 \times 10^4\,M^{-1}\,cm^{-1}$ it is possible to estimate lower value of quantum yield of $^3P3HT^*$ formation: $\varphi_T \geq 0.19$. To our knowledge, φ_T for P3HT has not been reported yet. In several works the triplet formation quantum yield for analogous polymer P3OT was determined, but the values are strongly different, for example $\varphi_T = 0.21$ in [33] and $\varphi_T = 0.77$ in [33,46]. The observed value of $^3P3HT^*$ quantum yield is close to the lower limit of the range of the reported values of triplet quantum yields of polythiophenes in solution [33].

5. Conclusions

Optical spectroscopy and nanosecond laser flash photolysis were applied to study photochemical properties of P3HT, $PC_{60}BM$ and their 1:1 mixture in argon-saturated toluene solution. Excitation of non-mixed solutions of P3HT and $PC_{60}BM$ leads to formation of corresponding triplet states. Excitation of P3HT/$PC_{60}BM$ mixture leads to effective energy transfer from $^3P3HT^*$ to ground state of fullerene with a formation of $^3PC_{60}BM^*$. For both triplet states the quantum yields, the absorption coefficients and the decay rate constants were estimated. Direct evidence of energetically favorable electron transfer from excited P3HT to $PC_{60}BM$ was not observed probably due to relatively small stabilization of radical-ion pair in nonpolar toluene used as a solvent leading to ultrafast back electron transfer and zero charge separation quantum yield.

Acknowledgments

The work was supported by Russian Foundation for Fundamental Research (grants No. 15-33-20421 and 14-03-00692), by the Ministry of Science and Education of Russian Federation (project 14.604.21.0078, registration number RFMEFI60414X0078) and by Scholarship of the President of Russian Federation SP-3596.2013.1. A.S.M. acknowledges the Saint-Petersburg State University for the financial support (postdoctoral fellowship No. 12.50.1562.2013). Also we thank Dr. M. Kazantsev from N.N. Vorozhtsov Institute of Organic Chemistry of the Siberian Branch of Russian Academy of Science for helpful discussions.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2015.07.002.

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